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IX. *On the Heat developed during the Combination of Acids and Bases.* By
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1. IT has been long known that chemical actions are in general accompanied by the evolution or abstraction of caloric. In most cases the change of temperature depends upon the result of the action of different causes, some of which tend to increase, and others to diminish the initial temperature of the reacting bodies. Thus, in the decomposition of a solution of carbonate of soda by concentrated sulphuric acid, the combination of the sulphuric acid with water and with the alcali are two distinct sources of heat, while the separation of the carbonic acid from the soda, and its evolution in the gaseous form, are equally distinct causes of a diminution of temperature. To estimate the influence of each of these circumstances in any particular instance is a problem of great difficulty; and we can only expect to accomplish its complete solution, by confining our investigations, in the first place, to these simpler cases, where the variations of temperature are produced by the operation of one single cause. For this reason, I have confined myself, in this preliminary inquiry, to the examination of the calorific phenomena which occur during the combination of acids and bases with each other, under the most favourable circumstances, for obtaining results free from complication.

2. The experiments to be hereafter described were all performed with very dilute solutions, by which means no correction was required for the heat evolved, when strong solutions of certain acids and alcalies are diluted. The method of operating is easily described. In separate glass vessels solutions of determinate weights were prepared, one containing the quantity of alcali whose power of generating heat was sought, and the other, a little more than the equivalent of

acid required to neutralize the alcali. After the liquids had acquired the same temperature, they were mixed together in the jar containing the alcali, and the increase of heat carefully observed by a delicate thermometer. This process was adopted from the facility of its execution and the uniformity of its results. It is, however, obvious, that a large portion of heat would be absorbed by the glass vessel ; and it was, therefore, necessary to establish, by a series of independent experiments, the corrections to be applied to the temperatures thus obtained.

3. As a basis to this whole investigation, the heat developed in the combination of nitric acid and potash was carefully determined. But before describing the method employed, I must anticipate an observation which will be afterwards proved, *viz.*, that the same amount of heat is developed when a given quantity of an alcali is united to an acid, whether the acid added be just sufficient to neutralize the alcali, or be considerably in excess.* The addition of a slight excess of acid does not, therefore, in any way interfere with the results, except in so far as it renders them more uniform and certain, by producing a rapid and complete neutralization of the alcali.

4. A cylindrical vessel of very thin brass was procured, capable of containing rather more than the quantity of liquid employed. Into this vessel was introduced the solution of caustic potash, the weight of which solution was about nine times greater than that of the dilute nitric acid destined to neutralize it. This vessel was so thin that we may assume, without any sensible error, its temperature to have been identical with that of its liquid contents. It weighed 6.63 grammes, which, assuming the specific heat of brass to be .094, is equivalent to 0.623 gr. water.

5. As the weights of the glass and mercury in the bulb and immersed portion of the tube of the thermometer were both unknown, I was obliged to have recourse to a direct experiment, in order to ascertain their equivalent of water. For this purpose, 30 grammes of water (the quantity of liquid usually employed) were introduced into the brass vessel, and the increase of its temperature carefully observed, when the thermometer, previously heated through a

* These observations, as well as others of a similar kind in subsequent parts of this paper, refer always to dilute solutions, such as are employed in these experiments.

certain number of degrees, was suddenly cooled by immersion in it. Denoting by t the loss of heat sustained by the thermometer, and by t' the temperature gained by the liquid, I obtained in different trials the following numbers :

| 1 | 2 | 3 |
|---------------------|---------------------|---------------------|
| $t = 59^{\circ}00,$ | $t = 69^{\circ}00,$ | $t = 72^{\circ}00.$ |
| $t' = 0^{\circ}90,$ | $t' = 1^{\circ}00,$ | $t' = 1^{\circ}15.$ |

Hence, we deduce for the value of the thermometer in grammes of water,

| 1 | 2 | 3 | Mean. |
|-------|-------|-------|-------|
| 0.47, | 0.45, | 0.49, | 0.47. |

6. From the last two results we may therefore conclude, that the brass vessel and thermometer, taken together, are equivalent to 1.09 gr. water.

7. A very important source of error in this and other similar investigations, where the variation of temperature of a liquid requires to be observed with the utmost precision, arises from the cooling influence of the surrounding air during the time occupied by the observation, which, in the experiments I am about to describe, amounted to nearly 1'. Where the increase of temperature does not exceed 2° or 3° Fah., the common method of cooling the liquid before the experiment begins, as many degrees below the temperature of the air as it will afterwards rise above it, may be employed with success ; but for greater increments of heat, this process is liable to a serious error, which it is necessary to avoid. In fact, on mixing the liquids together, the thermometer attains, in a very few seconds, almost its ultimate point of elevation, and it occupies at least four-fifths of the entire time in rising through the last half degree. As, therefore, the mixture continues much longer in the upper than in the lower half of its range of temperature, the method just described will necessarily yield results sensibly below the truth.* In practice, this error may be effectually obviated, by reducing the initial temperature of the liquid so far below the temperature of the air, that its final maximum may never reach higher than 2° F. above the same point.

* A similar observation has been made by M. Regnault in his recent and valuable memoir on the " Specific Heats of Simple and Compound Bodies" (Ann. de Chin. t. 63, p. 23) ; but the error thus induced he corrects by means of an interpolating formula.

8. The strongest nitric acid employed in these experiments contained 13.3 per cent. of real acid, and when one part of such an acid is diluted with nine parts of water, no sensible production of heat can be discovered by the most delicate thermometer. The corresponding solution of caustic potash, containing only 1.3 per cent. of alcali, was of course far beyond the limit of such sources of heat. That simple dilution exercised no influence on the result was further proved, by increasing the weight of the acid liquid, and diminishing that of the alkaline, while, at the same time, the quantities of acid and alcali in each, as also the total weight of both liquids, remained the same; yet such variations in the form of the experiment produced no change whatever in the elevation of temperature observed on mixing them.

9. Having discussed the corrections arising from the form of apparatus, I now proceed to give the details of the fundamental experiment, on the absolute amount of heat evolved in the union of nitric acid and potash. The general accuracy of these results was tested and confirmed by repeating the experiments in the form of a series, in which (the weight of the whole liquid remaining constant) the quantities of the combining substances were taken successively, in the proportions expressed by the numbers 1, 2, 4; and it will be seen that the corresponding increments of temperature bear a similar ratio to each other.

10. Into the brass vessel before described, a solution of caustic potash, containing .0882 gr. of alcali was introduced. It weighed 27.3 gr., which, added to 1.09 gr., the equivalent in water of the vessel and thermometer (6), makes the whole equal to 28.39 gr. water. The acid solution, in a small glass tube, weighed 2.83 gr., and contained .106 anhydrous nitric acid. Thermometer in air stood at 38° F.

| | | | | |
|---------------------------------|---|---|---|--------|
| Temp. of acid, | . | . | . | 38°.20 |
| „ alcaline solution, | . | . | . | 37°.00 |
| Mean temp. before mixture, | . | . | . | 37°.11 |
| Temp. after mixture, | . | . | . | 38°.75 |
| Increase in temp. (31.22 water) | . | | | 1°.64 |

11. The last experiment repeated. Ther. in air 39°.

| | |
|----------------------------------|--------|
| Temp. of acid, | 39°.00 |
| „ alcaline solution . | 37°.50 |
| Mean temp. before mixture | 37°.64 |
| Temp. after mixture, . . . | 39°.25 |
| Increase (31.22 gr. water) . . . | 1°.61 |

12. Alcaline solution weighed 27.2 gr., and contained .1765 gr. of pure potash, or double that in the last experiments. Acid solution weighed 2.85, gr. containing .212 anhydrous nitric acid. Ther. in air 39°.5.

| | |
|-------------------------------|--------|
| Temp. of acid, | 39°.00 |
| „ alcaline solution, . | 37°.00 |
| Mean temp. before mixture, | 37°.18 |
| Temp. after mixture, . . . | 40°.40 |
| Increase (31.14 water), . . . | 3°.22 |

13. Alcaline solution 26.85 gr., containing .353 potash; acid liquid 3.25 gr., containing .424 anhydrous nitric acid. Ther. in air 39.3°.

| | |
|------------------------------|--------|
| Temp. of acid | 39°.70 |
| „ alcaline solutions . | 34°.30 |
| Mean. Temp. before mixture, | 34°.86 |
| Temp. after mixture, . . . | 41°.45 |
| Increase (31.19 water) . . . | 6°.59 |

14. Reducing these results to the quantity of alcali (.353 gr.) used in last experiment, and to 30 gr. of water, we obtain the following numbers :

| 1 | 2 | 3 | 4 | Mean. |
|--------|--------|--------|--------|--------|
| 6°.83, | 6°.70, | 6°.68, | 6°.85, | 6°.76. |

15. This may be otherwise expressed, by stating that 1 gr. of potash, in combining with nitric acid, is capable of heating 85 gr. of water through 6°.76 of Fahrenheit's scale, or, which is the same thing, of heating 574.6 gr. of water through 1°. It must, however, be carefully observed, that in this experiment it

is not pure water, but a weak solution of nitrate of potash, which is actually heated ; and the above numbers would therefore require a further correction, in consequence of the difference between the specific heats of these liquids. This correction, however, must be extremely small, from the very dilute solutions obtained : it would probably be within the limit of the errors of observation.

16. Many of the subsequent experiments would have been performed with difficulty in a metallic vessel. I therefore substituted a pretty thick glass jar for the brass vessel, and both solutions were brought as nearly as possible to the temperature of the surrounding air, at the commencement of each observation. In this way, numerous experiments were easily performed, which yielded results comparable with each other, although all below the truth. It was, therefore, necessary to ascertain the absolute loss of heat when the experiment was performed in this way, and whether it was proportional to the elevation of temperature. For this purpose, solutions were prepared containing the same quantity of potash and nitric acid as in the experiments with the brass cylinder.

17. Alcaline solution 27 gr., containing .0882 gr. potash ; acid solution 3 gr., containing 1.06 nitric acid.

Temp. rose on mixture, 1°.45.

Another experiment gave 1°.45.

18. Alculine solution 27 gr., containing .1765 potash ; acid solution 3 gr., containing .212 nitric acid.

Temp. rose on mixture 2°.90.

Another experiment gave 2°.95.

19. Alcaline solution 27 gr., containing .353 potash ; acid solution 3 gr., containing .424 nitric acid.

Temp. rose on mixture 5°.8.

Another experiment gave 5°.8.

20. Alcaline solution 24 gr., containing .353 potash ; acid liquid 6 gr., containing .424 nitric acid.

Temp. on mixture rose to 5°.9.

21. Collecting these results, we obtain for the elevation of temperature of
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30 gr. of water, in a glass vessel, by the combination of .353 gr. potash with nitric acid :

| 1 | 2 | 3 | 4 | 5 | 6 | Mean. |
|-------|-------|-------|-------|-------|-------|--------|
| 5°.8, | 5°.8, | 5°.8, | 5°.9, | 5°.8, | 5°.9, | 5°.83. |

This number differs by 0.93° from the absolute quantity of heat before found, which is the loss of heat by this method of performing the experiment. It also appears from the coincidence of the results obtained with different proportions of alcali, that the loss of heat is proportional to the rise of temperature, and hence the necessary correction for this error is, in all cases, easily made.

22. When the base is insoluble in water, and slowly soluble in the acid, a new element enters into the observation, and requires to be estimated, viz., the cooling of the liquid during the prolonged duration of the experiment. In the observations last described, the thermometer attained its maximum in about 45" from the time the liquids were mixed, but in the solution of such substances, as magnesia or the oxide of zinc, not less than 2', or $2\frac{1}{2}'$ will elapse before the liquid becomes transparent, and the thermometer stationary. Even to complete the solution within this period, the liquid requires to be constantly stirred with a glass rod. This circumstance renders these results less precise than those in which the combination occurs instantaneously; but the amount of error thus produced may be estimated, by repeating the same experiment in precisely the same manner, with a solution of caustic potash, containing exactly the quantity of alcali (as deduced by calculation from the foregoing experiments) which should produce the same elevation of temperature as had been obtained with the slowly soluble base. The difference between the increase of heat actually found, and that deduced from calculation, will be equal to the loss of caloric occasioned by the stirring, and length of the experiment; and consequently the required correction for the number obtained by observation. The precise value of this correction will be given hereafter.

23. The general conclusions which I shall endeavour to establish in the subsequent part of this communication, may be enunciated in the form of the three following laws :

LAW 1.—*The heat developed during the union of acids and bases is determined by the base and not by the acid; the same base producing, when*

combined with an equivalent of different acids, nearly the same quantity of heat; but different bases a different quantity.

LAW 2.—*When a neutral is converted into an acid salt, by combining with one or more atoms of acid, no change of temperature occurs.*

LAW 3.—*When a neutral is converted into a basic salt, by combining with an additional proportion of base, the combination is accompanied with the evolution of heat.*

24. To the first of these laws important exceptions are presented by the peroxide of mercury among the bases, and by the hydrocyanic, and probably the carbonic acid, among the acids; and it is not improbable that more extended investigations will lead to the discovery of other exceptions. The second law has been established by numerous experiments, and can scarcely be said to be liable to any well-marked exception; but I feel much less confidence in enunciating the third, as a general principle, from the very limited number of cases of soluble subsalts in which it was possible to verify its accuracy.

25. In order to obtain results of as much uniformity as possible, the standard alkaline solution was always mixed with rather a greater quantity of acid than was necessary to neutralize it.* The combination was thus effected more rapidly and certainly, than if an attempt had been made to form an exactly neutral compound. That this excess of acid did not produce any sensible difference in the result, will be rendered evident, when the experiments are examined, which will be hereafter cited, in illustration of law second; and, indeed, if no basic compound existed, the numbers obtained were identical, whether an equivalent of base was neutralized by an excess of acid, or a like equivalent of acid neutralized by an excess of base. I have arranged, in distinct tables, the increments of temperature obtained by combining an equivalent of each base with the acids. The equivalents taken were .353 grammes potash, .234 gr. soda, .129 gr. ammonia, .572 gr. barytes, .213 gr. lime, .154 gr. magnesia, .301 gr. oxide of zinc, .834 gr. oxide of lead, .870 gr. oxide of silver, and .810 gr. peroxide of

* In the cases of the phosphoric and arsenic acids, the quantity of acid was just sufficient to convert the alcali into the common phosphate and arseniate; that is, half an equivalent of acid for an equivalent of base. The reason of this will appear again (55). The number for chromic acid is only deduced from an indirect experiment upon the bichromate of potash.

mercury. The entire weight of the solution, after the mixture was made, amounted in every instance to 30 grammes. In the first four tables, the first column of numbers contains the elevation of the thermometer actually observed; and the second, the result corrected for the loss of heat, occasioned by the mode of performing the experiment (21).

26. TABLE I.—*Potash.*

| ACID. | FOUND. | CORRECTED. | DIFFERENCE FROM MEAN. |
|-------------------------|-----------|------------|-----------------------|
| Sulphuric, | 6°.30 | 7°.32 | + 0°.80 |
| Nitric, | 5.83 | 6.76 | + 0.24 |
| Phosphoric, | 5.70 | 6.61 | + 0.09 |
| Arsenic, | 5.70 | 6.61 | + 0.09 |
| Hydrochloric, | 5.65 | 6.56 | + 0.04 |
| Hydriodic, | 5.80 | 6.74 | + 0.22 |
| Boracic, | 5.60 | 6.50 | - 0.02 |
| Chromic, | 5.55 | 6.46 | - 0.06 |
| Oxalic, | 5.70 | 6.62 | + 0.10 |
| Acetic, | 5.50 | 6.39 | - 0.13 |
| Formic, | 5.50 | 6.39 | - 0.13 |
| Tartaric, | 5.25 | 6.10 | - 0.42 |
| Citric, | 5.25 | 6.10 | - 0.42 |
| Succinic, | 5.25 | 6.10 | - 0.42 |
| Mean, | | 6.52 | |

27. TABLE II.—*Soda*.

| ACID. | FOUND. | CORRECTED. | DIFFERENCE FROM MEAN. |
|-------------------------|-----------|------------|-----------------------|
| Sulphuric, | 6°.40 | 7°.44 | + 0°.96 |
| Nitric, | 5.55 | 6.45 | - 0.03 |
| Phosphoric, | 5.55 | 6.45 | - 0.03 |
| Arsenic, | 5.60 | 6.50 | + 0.02 |
| Hydrochloric, | 5.80 | 6.74 | + 0.26 |
| Hydriodic, | 5.70 | 6.62 | + 0.14 |
| Boracic, | 5.80 | 6.74 | + 0.26 |
| Oxalic, | 5.75 | 6.68 | + 0.20 |
| Acetic, | 5.45 | 6.34 | - 0.14 |
| Tartaric, | 5.10 | 5.93 | - 0.55 |
| Citric, | 5.10 | 5.93 | - 0.55 |
| Succinic, | 5.10 | 5.93 | - 0.55 |
| Mean, | | 6.48 | |

28. TABLE III.—*Barytes*.

| ACID. | FOUND. | CORRECTED. | DIFFERENCE FROM MEAN. |
|-------------------------|-----------|------------|-----------------------|
| Nitric, | 5°.90 | 6°.85 | + 0°.10 |
| Hydrochloric, | 5.85 | 6.79 | + 0.04 |
| Hydriodic, . . . , . . | 6.00 | 6.97 | + 0.22 |
| Acetic, | 5.50 | 6.39 | - 0.36 |
| Mean, | | 6.75 | |

29. TABLE IV.—*Ammonia.*

| ACID. | FOUND. | CORRECTED. | DIFFERENCE FROM MEAN. |
|-------------------------|-----------|------------|-----------------------|
| Sulphuric, | 5°.45 | 6°.34 | + 0°.82 |
| Nitric, | 4.80 | 5.58 | + 0.06 |
| Arsenic, | 4.90 | 5.69 | + 0.17 |
| Hydrochloric, | 4.80 | 5.58 | + 0.06 |
| Hydriodic, | 4.80 | 5.58 | + 0.06 |
| Oxalic, | 4.90 | 5.69 | + 0.17 |
| Acetic, | 4.70 | 5.47 | - 0.05 |
| Tartaric, | 4.40 | 5.11 | - 0.41 |
| Citric, | 4.35 | 5.05 | - 0.47 |
| Succinic, | 4.40 | 5.11 | - 0.41 |
| Mean, | | 5.52 | |

30. The remainder of the bases examined, being either insoluble or very slightly soluble in water, were added in the solid state to the acid solution, whose weight was always so adjusted as, together with that of the base, to be equal to 30 grammes. The bases were all taken in the anhydrous state, except lime, which dissolves with extreme difficulty even in the dilute acids, unless previously converted into a hydrate. The experiments performed with these bases occupied from 80" to 100" longer than those with the soluble alcalis. This renders the application of a new correction necessary. The method of determining the amount of this correction has been already explained (23). In the remaining tables, the first column contains the result as found by experiment; the second, the duration of the observation; the third, the correction applied for the heat lost thereby; the fourth, the corrected result; and the fifth, the difference from the mean.

31. TABLE V.—*Magnesia.*

| ACID. | FOUND. | TIME. | COR. TIME. | CORRECTED. | DIFFERENCE FROM MEAN. |
|------------------|-----------|-----------|------------|------------|-----------------------|
| Sulphuric, . . . | 7°.00 | 2' | 0°.30 | 8°.48 | + 0°.24 |
| Nitric, . . . | 6.70 | 2 | 0.30 | 8.13 | + 0.11 |
| Hydrochloric, | 6.60 | 2 | 0.30 | 8.11 | — 0.13 |
| Mean, . . . | | | | 8.24 | |

32. TABLE VI.—*Lime.*

| ACID. | FOUND. | TIME. | COR. TIME. | CORRECTED. | DIFFERENCE FROM MEAN. |
|---------------|-----------|-------------------|------------|------------|-----------------------|
| Nitric, . . . | 5°.95 | 1 $\frac{1}{2}$ ' | 0°.25 | 7°.20 | + 0°.10 |
| Hydrochloric, | 5.85 | 1 $\frac{1}{2}$ | 0.25 | 7.08 | — 0.02 |
| Acetic, . . . | 5.80 | 1 $\frac{1}{2}$ | 0.25 | 7.03 | — 0.07 |
| Mean, . . . | | | | 7.10 | |

33. TABLE VII.—*Oxide of Zinc.*

| ACID. | FOUND. | TIME. | COR. TIME. | CORRECTED. | DIFFERENCE FROM MEAN. |
|------------------|-----------|-----------|------------|------------|-----------------------|
| Sulphuric, . . . | 4°.45 | 2' | 0°.20 | 5°.40 | + 0°.49 |
| Nitric, . . . | 3.90 | 2 | 0.20 | 4.76 | — 0.15 |
| Hydrochloric, | 4.00 | 2 | 0.20 | 4.88 | — 0.03 |
| Hydriodic, . | 3.50 | 4 | 0.45 | 4.59 | — 0.32 |
| Mean, . . . | | | | 4.91 | |

34. TABLE VIII.—*Oxide of Lead.*

| ACID. | FOUND. | TIME. | COR. TIME. | CORRECTED. | DIFFERENCE FROM MEAN. |
|---------------|-----------|-----------|------------|------------|-----------------------|
| Nitric, . . . | 3°.45 | 2' | 0°.15 | 4°.18 | + 0°.20 |
| Acetic, . . . | 2.95 | 3 | 0.30 | 3.78 | — 0.20 |
| Mean, . . . | | | | 3.98 | |

35. The oxide of silver gave, with nitric acid, an increase of temperature of 2°.7 corresponding, when corrected, to an actual elevation of 3°.23.

36. To render the numbers in each table strictly comparable with one another, would require a minute investigation of the influence of every possible source of a variation of temperature in the experiments; such are, differences in the specific heats of the solutions formed, alterations in the density of the liquids after mixture, &c. However, from very dilute solutions being employed, and also, from the results being identical when the strength of the solutions was greatly varied (9), it is probable that the errors arising from such causes could not amount, in most cases, to more than a few hundredths of a degree. Taking, therefore, the results as they appear in the tables, it will be found on examination, that they are in accordance with Law 1, (24). If we refer to the first, second, and fourth tables, as being the most extensive, from the large number of soluble compounds formed by potash, soda, and ammonia, it will be observed, that the sulphuric acid develops from 0°.8 to nearly 1° more than the mean heat given by the other acids, while the tartaric, citric, and succinic acids fall from 0°.4 to 0°.55 short of the same. A minute investigation of the influence of the disturbing sources of heat will, no doubt, discover the cause of these discrepancies; the high numbers for sulphuric acid are probably connected with that acid's well-known property of developing much heat when combined with successive atoms of water. All the other acids develop very nearly the same amount of heat in combining with the same base; the greatest divergences from the mean quantity being in the case of potash, + 0°.24, and — 0°.13; in that of soda, + 0°.26,

— 0°.14 ; and in that of ammonia + 0°.17 and — 0°.05. These differences are almost within the limits of the errors of experiment. In the other tables a similar agreement will be found to exist. Indeed the sulphuric acid does not exhibit in them so wide a discordance from the other acids as before. I must, however, remark that the numbers for the insoluble bases are scarcely so exact as those which are contained in the first four tables.

37. Whether the base be soluble or insoluble in water, the increments of temperature obtained, by combining the same base with different acids, may be compared with each other ; but if we wish to discover the relations subsisting between the temperatures developed by different bases, it becomes necessary to take into consideration the heat absorbed by the insoluble bases, in passing from the solid to the fluid state. I am not at present acquainted with any method whereby the heat thus abstracted can be estimated. But the numbers for the insoluble bases, from this cause, will be all too low. We may, therefore, arrange the bases in the following order, in respect to their power of developing heat when combining with the acids ; but this arrangement is liable to be disturbed when the value of the unknown quantities shall be determined. It must also be recollectcd that the potash, soda, barytes and lime were in the state of hydrates before mixture, while the magnesia, oxide of zinc, oxide of lead, and oxide of silver were anhydrous.

| | | | | | |
|------------------|---|---|---|---|--------------|
| Magnesia, | . | . | . | . | 8°.24 + x |
| Lime, | . | . | . | . | 7.10 + x' |
| Barytes, | . | . | . | . | 6.75 |
| Potash, | . | . | . | . | 6.52 |
| Soda, | . | . | . | . | 6.48 |
| Ammonia, | . | . | . | . | 5.52 |
| Oxide of Zinc, | . | . | . | . | 4.91 + x'' |
| Oxide of Lead, | . | . | . | . | 3.98 + x''' |
| Oxide of Silver, | . | . | . | . | 3.23 + x'''' |

38. The peroxide of mercury has given results altogether at variance with the preceding. It develops with the nitric and acetic acids nearly the same quantity of heat, but with the hydracids the most singular anomalies occur, as will appear in the next table.

39. TABLE IX.—*Peroxide of Mercury.*

| ACID. | FOUND. | TIME. | CORR. TIME. | CORRECTED. |
|-------------------------|--------|-------|-------------|------------|
| Nitric, | 1°.20 | 2' | 0°.05 | 1°.27 |
| Acetic, | 1.20 | 2 | 0.05 | 1.27 |
| Hydrochloric, | 3.80 | 2 | 0.20 | 4.65 |
| Hydrocyanic, | 5.85 | 2 | 0.25 | 7.10 |
| Hydriodic, | 9.20 | 3 | 0.60 | 11.40 |

40. To the last number some objection may be made, as a large excess of hydriodic acid was used to prevent the formation of the insoluble periodide of mercury; but even if we omit it altogether, the other parts of the table exhibit singular discrepancies. It is probable that a more extended investigation will discover other metallic oxides, resembling the peroxide of mercury, in yielding different quantities of heat, when they combine with the hydracids.

41. The hydrocyanic acid stands not less apart from the other acids than the oxide of mercury from the rest of the bases, in its development of heat when forming compounds; and it is remarkable that no analogous property appears with the hydrochloric and hydriodic acids. The hydrocyanic acid used in these experiments was perfectly pure: it was employed immediately after being rectified over chalk, and had no action on vegetable colours. I have collected together the elevations of temperature produced by it, and contrasted them with the mean quantities of heat given by the other acids with each base.

| BASE. | HYDROCYANIC ACID. | MEAN OF OTHER ACIDS. | DIFFERENCE. |
|----------------------------|-------------------|----------------------|-------------|
| Potash, | 1°.45 | 6°.52 | 5°.07 |
| Soda, | 1.45 | 6.48 | 5.03 |
| Barytes, | 1.68 | 6.75 | 5.07 |
| Ammonia, | 0.51 | 5.52 | 5.01 |
| Peroxide of Mercury, . . . | 7.10 | | |

42. Thus the hydrocyanic acid develops with potash, soda, barytes, and ammonia, 5° less than the other acids. On the other hand, it yields no less than $7^{\circ}.1$ in combining with the peroxide of mercury, while the oxyacids produce with the same base, only $1^{\circ}.27$.

43. I now proceed to cite a few experiments in illustration of Law 2; viz., that during the conversion of a neutral into an acid salt, no evolution of heat occurs.

44. 23 gr. of a solution of caustic potash, containing .353 gr. of alkali, were mixed with 7 gr. of a solution of oxalic acid, containing .271 gr. (or 1 equiv.) of acid.

Temp. after mixture rose $5^{\circ}.7$.

45. 31 gr. of a solution of neutral oxalate of potash, containing .624 gr. of the salt, were mixed with 9 gr. of a solution of oxalic acid, containing .271 gr. (1 equiv.) acid.

Temp. after mixture rose $0^{\circ}.0$.

46. The solution of binoxolate of potash, obtained in last experiment, was mixed with 18 gr. of the solution of oxalic acid (2 equiv.)

Temp. rose after mixture $0^{\circ}.15$.

After some time, crystals of quadroxalate of potash began to form, which accounted for the slight elevation of temperature.

47. On adding to a solution of sulphate of potash a second atom of sulphuric acid, the temperature of the mixture rose only $0^{\circ}.1$, although the combination of the first atom had produced $6^{\circ}.3$ of heat.

48. Similar results were obtained with the oxalate, tartrate, and acetate of soda, when converted into the corresponding supersalts ; and by neutralizing these acid salts with the base, the same heat was invariably produced as if the excess of acid had existed in a free state. I may cite particularly the case of the bichromate of potash, which gave, when converted into the neutral chromate, a quantity of heat corresponding with that developed by the acids in general with potash, viz., $6^{\circ}.45$. In verifying this principle, care must be taken to select examples where all the compounds are soluble salts ; otherwise, the latent heat extricated by the solid precipitate would interfere with, and complicate the

result. It is for this reason that the formation of the bitartrate of potash is accompanied by heat, although none is evolved when the neutral tartrate of soda combines with a second atom of acid.

49. As a farther illustration of the same principle, I am unwilling to omit the description of an interesting experiment, although its complete explanation involves the consideration of a class of phenomena which I have carefully excluded from the present communication. Three solutions were prepared, each containing 25 gr. of liquid; the first, holding in solution .353 gr. of pure potash; the second, .520 gr. of carbonate of potash; and the third, .683 gr. of bicarbonate of potash; consequently the amount of real alcali the same in all. They were then separately neutralized by 5 gr. of a solution of nitric acid, containing a considerable excess of acid, and the two latter solutions were well stirred, to expel, as far as possible, the carbonic acid gas before the final temperature was observed. The elevations of temperature were, for

| | DIF. |
|--------------------------------|--------------|
| Pure Potash, | 5°.8 |
| Carbonate of Potash, | 1.7 — 4.1 |
| Bicarbonate of Potash, | 0.4 1.3 |

50. Thus we see that the effect of separating the first atom of carbonic acid, in the gaseous state, from its combinations with the alcali, was to cause the disappearance of 4°.1 of heat; while the separation of the second atom, and its complete expulsion in the gaseous state, produced a further diminution of temperature of only 1°.3. In these observations, two distinct sources of an absorption of caloric exists; one, the separation of the chemical compound into its constituents; the other, the change of one of those constituents from the liquid to the gaseous state. Had both causes acted equally on the second as on the first atom of carbonic acid, we should have obtained with the bicarbonate, as great a diminution of temperature as had occurred with the carbonate, or the thermometer would have sunk 2°.4 instead of rising .4°. But the conversion of the second atom of carbonic acid into the gaseous state is completely effected, while a considerable portion of the first atom remains dissolved in the liquid; and consequently, the striking difference in the result can only be accounted for, on the principle stated in the second law, that the combination, or separation of

the second atom of carbonic acid is attended with no evolution or abstraction of heat.

51. The tribasic, phosphoric, and arsenic acids, in their combinations with the fixed alcalis, present a slight divergence from this law, and at the same time, give results closely coincident with each other. In the following table, the increments of temperature are exhibited which were observed, when solutions, containing the compounds denoted by the first and second members of the expression, were mixed together. The symbol NaO corresponds, as before, to .234 gr. soda, and the entire weight of the solution was 30 grammes.

| | FOUND. | CORRECTED. |
|---|----------------------|----------------------|
| $(NaO + \frac{1}{2}P_2O_5) + \frac{1}{4}P_2O_5$ | . . . $0^{\circ}.40$ | . . . $0^{\circ}.46$ |
| $(NaO + \frac{3}{4}P_2O_5) + \frac{1}{4}P_2O_5$ | . . . $0^{\circ}.30$ | . . . $0^{\circ}.35$ |

52. In other words, the combination of the common phosphate of soda with half as much acid as it already contains produces an increment of temperature of $0^{\circ}.46$; and its complete conversion into the biphenophate, a farther increase of $0^{\circ}.35$. Similar numbers were obtained with the arsenic acid.

| | FOUND. | CORRECTED. |
|---|----------------------|----------------------|
| $(NaO + \frac{1}{2}As_2O_5) + \frac{1}{4}As_2O_5$ | . . . $0^{\circ}.40$ | . . . $0^{\circ}.46$ |
| $(NaO + \frac{3}{4}As_2O_5) + \frac{1}{4}As_2O_5$ | . . . $0^{\circ}.35$ | . . . $0^{\circ}.40$ |

54. The same acid gave with potash,

| | FOUND. | CORRECTED. |
|--|----------------------|----------------------|
| $(KO + \frac{1}{2}As_2O_5) + \frac{1}{2}As_2O_5$ | . . . $0^{\circ}.80$ | . . . $0^{\circ}.93$ |

55. From these experiments it follows, that during the conversion of the common alkaline phosphates and arseniates into supersalts, a quantity of heat is evolved, which is about one-seventh part of that produced during the formation of those salts themselves. As, however, the alkaline phosphates and arseniates are not strictly neutral in composition, and their solutions have an alkaline reaction, it is, perhaps, scarcely correct to adduce them as exceptions to Law 2. The pyrophosphoric acid, in similar circumstances, scarcely produces any heat;

resembling, in this and its other thermal properties, the ordinary acids. Denoting the pyrophosphoric acid by Pyr. we have,

| | FOUND. | CORRECTED. |
|--|-------------|------------|
| $(\text{NaO} + \frac{1}{2} \text{Pyr}_2\text{O}_5) + \frac{1}{4} \text{Pyr}_2\text{O}_5$ | 0°.15 . . . | 0°.17 |
| $(\text{NaO} + \frac{3}{4} \text{Pyr}_2\text{O}_5) + \frac{1}{4} \text{Pyr}_2\text{O}_5$ | 0°.00 . . . | 0°.00 |

55. The formation of the alkaline subphosphates and subarseniates, by the direct union of the common phosphates and arseniates, with an additional equivalent of base, is accompanied with a definite evolution of heat. On adding to solutions of these salts, containing the equivalents of alcali before referred to (NaO , .234 gr. KO , .353 gr.), alkaline solutions having half as much base as was already in the salts themselves, I obtained very uniform results.

| | FOUND. | CORRECTED. |
|--|------------|------------|
| $(\text{NaO} + \frac{1}{2} \text{P}_2\text{O}_5) + \frac{1}{2} \text{NaO}$ | 1°.7 . . . | 1°.97 |
| $(\text{NaO} + \frac{1}{2} \text{As}_2\text{O}_5) + ^1\text{NaO}$ | 1°.7 . . . | 1°.97 |
| $(\text{KO} + \frac{1}{2} \text{As}_2\text{O}_5) + \frac{1}{2} \text{KO}$ | 1°.7 . . . | 1°.97 |
| $(\text{NaO} + \frac{1}{2} \text{Pyr}_2\text{O}_5) + \frac{1}{2} \text{NaO}$ | 0°.1 . . . | 0°.12 |

56. That the heat produced was connected with the formation of the subsalt, appears distinctly from the circumstance, that a further addition of alcali was not attended with any increase of temperature. The absence of any heat in the case of the pyrophosphate of soda is easily explained on the same principle, as Graham has shown that no subpyrophosphate of soda exists.

57. The formation of these subsalts exercises a remarkable influence on the quantities of heat developed, when the base is neutralized by successive portions of acid. In ordinary cases, the heat evolved in this way is proportional to the quantity of acid added. Thus, on mixing a solution of pure potash with one-fourth, one-half, &c., an equivalent of nitric acid, the elevations of temperature will be one-half, one-fourth, &c. of what is observed when the alcali is completely neutralized. And the same principle I find to hold good, when successive portions of the phosphoric (tribasic) and arsenic acids are added to solutions of the pure alcalis, till the subsalts are formed; but, after that point, a very different law is followed, as will be seen in the next tables:

| | | FOUND. | CORRECTED. |
|------|--|--------|------------|
| I. | $\text{NaO} + \frac{1}{3}\text{P}_2\text{O}_5$, | 4°.65 | 5°.40 |
| | $(\text{NaO} + \frac{1}{3}\text{P}_2\text{O}_5 + \frac{1}{6}\text{P}_2\text{O}_5)$, | 0.90 | 1.04 |
| II. | $\text{NaO} + \frac{1}{3}\text{As}_2\text{O}_5$, | 4°.75 | 5°.51 |
| | $(\text{NaO} + \frac{1}{3}\text{As}_2\text{O}_5) + \frac{1}{6}\text{As}_2\text{O}_5$, | .85 | .99 |
| III. | $\text{KO} + \frac{1}{3}\text{As}_2\text{O}_5$, | 4.80 | 5°.57 |
| | $(\text{KO} + \frac{1}{3}\text{As}_2\text{O}_5) + \frac{1}{6}\text{As}_2\text{O}_5$, | .90 | 1.04 |

58. Had the evolutions of heat corresponded with the additions of acid the second numbers would have been one-half of the first in each set of experiments. Hence, the increments of temperature for equal portions of acid are nearly as 2.5 : 1, before and after the formation of the subsalt. The pyrophosphoric acid, on the contrary, presents no similar irregularity, developing equal increments of heat, for equal additions of acid, till the pyrophosphate of soda ($\text{NaO} + \frac{1}{2}\text{Pyr}_2\text{O}_5$) is formed.

59. It may, perhaps, be premature, from such imperfect and limited data, to offer any general observations on the preceding experiments; but I shall, nevertheless, venture to show the accordance of laws second and third, with those general views of the constitution of the salts which have been so ably illustrated by Graham. The conversion of a neutral into an acid salt being in reality the formation of a double salt, is not accompanied by any disengagement of heat; because such combinations as the latter do not evolve heat. No caloric is extricated when the tartrates of potash and soda unite; and, consequently, none ought to be given off, when the tartrate of soda is combined with the tartrate of water. But, on the other hand, heat is disengaged when the base in the tartrate of water is replaced by soda; because soda, in its combinations with the acids, evolves much more heat than water. How far the heat evolved in the formation of the different hydrated acids may be the same, is an interesting question not yet determined; but there can be little doubt that water holds a very low rank among the bases, in reference to its power of generating heat when combining with the acids. On the same principles, and again referring to the observations of Graham, we can understand the cause of the evolution of heat during the

conversion of the neutral phosphates and arseniates into basic salts. In reality, an equivalent of water is here again replaced by an equivalent of alkali, just as occurs in the direct combinations of the acids and alkalis.*

* When the experiments detailed in the foregoing paper were almost completed, I received the 6th No. of *Poggendorff's Annalen*, for 1840, containing the first part of a valuable Memoir, by M. Hess, entitled "Thermo-chemical Researches." The experiments detailed by M. Hess refer principally to the heat developed when sulphuric acid and water combine together—a subject not touched upon in the present paper. He has, however, extended his inquiry to the heat evolved during the combination of sulphuric acid with potash, soda, ammonia, and lime; and also of hydrochloric acid with potash, soda, and ammonia. But the results obtained by M. Hess cannot be immediately compared with those given in this communication, as his experiments were performed with stronger acids, which disengaged heat when diluted with water. The quantity of heat thus extricated, M. Hess has shown to be the same, whether the acid and water be mixed together in presence of a base or alone; and he has likewise furnished accurate data, by means of which the heat derived from this source, in his experiments, may be estimated. Now, assuming with him, as a term of comparison, the number of grammes of water which would be heated through 1° centigrade, by saturating with each alkali 1 gramme of sulphuric acid, or the corresponding equivalent (0.908 gr.) of hydrochloric acid—all taken in the state of very dilute solutions—we deduce from the foregoing tables the numerical results in the first of the following columns; while those in the second are derived from the memoir of M. Hess :

| | TABLES. | HESS. | | | | | | | | | | | | | | | |
|------------------------------|--|---------|-----------|-----|-----------|-----|-------|-----------|-----|-----------|-----|----------|-----------|-----|-----------|-----|--|
| Sulphuric Acid with . . . | <table border="0"> <tr> <td style="padding-right: 10px;">Potash,</td><td style="text-align: right;">.</td><td style="text-align: right;">407</td><td style="text-align: right;">.</td><td style="text-align: right;">406</td></tr> <tr> <td style="padding-right: 10px;">Soda,</td><td style="text-align: right;">.</td><td style="text-align: right;">413</td><td style="text-align: right;">.</td><td style="text-align: right;">411</td></tr> <tr> <td style="padding-right: 10px;">Ammonia,</td><td style="text-align: right;">.</td><td style="text-align: right;">352</td><td style="text-align: right;">.</td><td style="text-align: right;">403</td></tr> </table> | Potash, | | 407 | | 406 | Soda, | | 413 | | 411 | Ammonia, | | 352 | | 403 | |
| Potash, | | 407 | | 406 | | | | | | | | | | | | | |
| Soda, | | 413 | | 411 | | | | | | | | | | | | | |
| Ammonia, | | 352 | | 403 | | | | | | | | | | | | | |
| Hydrochloric Acid with . . . | <table border="0"> <tr> <td style="padding-right: 10px;">Potash,</td><td style="text-align: right;">.</td><td style="text-align: right;">364</td><td style="text-align: right;">.</td><td style="text-align: right;">362</td></tr> <tr> <td style="padding-right: 10px;">Soda,</td><td style="text-align: right;">.</td><td style="text-align: right;">373</td><td style="text-align: right;">.</td><td style="text-align: right;">368</td></tr> <tr> <td style="padding-right: 10px;">Ammonia,</td><td style="text-align: right;">.</td><td style="text-align: right;">310</td><td style="text-align: right;">.</td><td style="text-align: right;">318</td></tr> </table> | Potash, | | 364 | | 362 | Soda, | | 373 | | 368 | Ammonia, | | 310 | | 318 | |
| Potash, | | 364 | | 362 | | | | | | | | | | | | | |
| Soda, | | 373 | | 368 | | | | | | | | | | | | | |
| Ammonia, | | 310 | | 318 | | | | | | | | | | | | | |

It is very satisfactory to observe how closely these numbers agree with each other, with the single exception of that which expresses the heat evolved when sulphuric acid and ammonia combine. The cause of this discrepancy I have endeavoured in vain to discover; but it probably depends upon some condition in the experiment of M. Hess, which may have escaped my observation.